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Analyses of Paint Media

John Mills and Raymond White

We present here in tabular form some of the results on analysis of paint media obtained by gas-chromatography from samples from National Gallery paintings. They are not all free from ambiguity, as might be expected from paintings which sometimes have a long history of reworkings and treatments of various kinds, neither has it been possible in all cases to follow up these doubtful results with testing by other means such as staining of cross-sections. They are nonetheless recorded here for possible future reference.

The analyses are based on determining the fatty acid composition of the paint sample after it has been saponified with alkali and the acids converted to their methyl esters. The method has been described in two papers (1,2), and has also seen application in other laboratories besides our own, notably at the Louvre (3,4). Put very briefly, the presence of a large amount of one component, azelaic acid, indicates the presence of drying oil while the presence of only a small proportion of this compound relative to significant amounts of other fatty acids such as palmitic and stearic acids indicates the presence of egg fats. The absence of significant quantities of these latter compounds implies the absence of both these media and hence (in the context of easel painting) of the presence of some other tempera medium such as glue. This can then be separately tested for.

The presence of both drying oil and egg-yolk in a sample results in a chromatogram with an intermediate level of azelaic acid. When such an intermediate level is found, therefore, the presence of both media is inferred. This is not very satisfactory evidence, though, and it is desirable to follow it up with other tests.

If the medium is thought to be oil then the ratios of the amounts of palmitic and stearic acids (the P/S ratios) are measured to give an indication of the probable identity of the oil—walnut, linseed, or poppy. It should be mentioned here that we now know that the P/S ratio for another possible oil, hempseed, falls within the same range as that of walnut and this introduces another element of uncertainty. However, this is an oil which has probably been only rather rarely used in painting as it tends to have a bright green colour when first expressed, but it is a possibility which must be born in mind. Obviously mixtures of oils will produce intermediate P/S ratios and we can therefore be most confident about our results when they lie at the two extremes of the range found, i.e. below 2.0 (linseed) and above about 4.0 (poppy).

Some of the paintings examined gave very consistent P/S ratios (e.g. Gossaert's *Adoration of the Kings* and Titian's *Vendramin Family*) while others, even when they seemed to be in oil alone, gave very variable ones (*Master of the Life of the Virgin*, Nos.252 and 253).

References

1. J. S. Mills, 'The Gas-Chromatographic Examination of Paint Media Part I. Fatty acid Composition and Identification of Dried Oil Films,' *Studies in Conservation*, 11 (1966), 92-106.
2. John S. Mills, and Raymond White, 'The Gas-Chromatographic Examination of Paint Media. Some Examples of Medium Identification in Painting by Fatty Acid Analysis,' *Conservation and Restoration of Pictorial Art*, (ed. N. Brommelle and P. Smith) Butterworths (1976), 72-77.
3. J.-P. Rioux, Note sur l'Analyse de quelques Enduits provenant de Peintures francaises des XVII et XVIII Siècles, Laboratoires de Recherche des Musées de France, *Annales*, 1973, 35-43.
4. S. Delbourgo and J.-P. Rioux, Contribution a l'Étude de la Matière picturale des Impressionistes, *ibid*, 1974, 34-42.

Artist	Picture	Date	Sample	Medium	P/S	Oil type	Note	
Giovanni Bellini	The Madonna of the Meadow NG 599	End of 15th C.	1. Unpigmented priming on ground 2. Blue underpaint	Egg + trace oil? Egg + oil?				
Giovanni Bellini	The Agony in the Garden NG 726	c. 1465	Blue paint of trees	Egg				
Cima da Conegliano	S. Sebastian NG 4946	End of 15th C.	1. Grey background	Oil	1.55-1.96	Linseed	1	
			2. White loincloth	Oil	1.67	Linseed		
	A Male Saint NG 4945	End of 15th C.	1. Grey background	Oil	1.84	Linseed		
			2. Blue robe	Oil	1.65	Linseed		
			3. Pale blue spandrel	Oil	1.61	Linseed		
			4. Red robe	Oil	1.51	Linseed		
Girolamo da Treviso	Madonna and Child with SS. and Donor NG 623	2nd quarter 16th C.	1. Saint's red robe, L.H.S. 2. Grey base of pillar	Oil Oil	1.6 2.16-2.40	Linseed Walnut?	2	
Ascribed to Fra Filippo Lippi	Virgin and Child. NG 3424	15th C.	1. Brown scumble 2. Pink stripe, L.H.S. 3. Blue Virgin's robe, top layer 4. ditto, lower layer 5. White, Virgin's dress 6. Green, T.R.H. corner	Egg + oil? Egg + oil? Egg Egg Egg + trace oil? Egg			3	
Andrea Mantegna	Introduction of the Cult of Cybele to Rome NG 902	c. 1505	1. Red-brown, top 2. Grey, R.H. edge 3. White stripe of pillar	Glue Glue Glue			4	
Melone	The walk to Emmaus. NG 753	1st quarter 16th C.	1. Brown tree trunk Top L.H.S. 2. Reddish paint, central figure	Oil Oil	2.6 2.1	Walnut ?		
Evangelista Preda or Associate of Leonardo da Vinci	An angel in Red with a Lute NG 1662	End 15th C.	1. Dark grey overpaint L.H.S. 2. Lighter grey under 1 3. Grey-white of centre niche 4. Red of robe 5. Dark grey of niche, top L.H.S. 6. Brown edge of wing, R.H.S. 7. Red-brown under grey, R.H.S.	Oil Oil Oil Oil Oil Oil Oil	2.72 3.05 3.01 2.06 2.65 2.64 2.43	Walnut Walnut Walnut ? Walnut Walnut Walnut	5	
	Sassetta	The Whim of S. Francis to become a Soldier. NG 4757	2nd quarter 15th C.	1. White, R.H. column 2. Dark red glaze over silver 3. Blue sky 4. Green chest	Egg Egg Egg Egg			6
	Titian	Venus and Adonis NG 34	Mid 16th C.	1. Brown on bow 2. Adonis's leg	Oil Oil	1.52 2.14	Linseed Linseed	
		The Vendramin Family NG 4452	Mid 16th C.	1. Deep red glaze central profile figure 2. Blue sky 3. Boy's red stocking 4. Maroon robe, old man centre 5. Black boy's robe L.H.S. 6. Ermine sleeve, old man	Oil Oil Oil Oil Oil Oil	2.80 2.40 2.60 2.90 2.60 2.50	Walnut Walnut Walnut Walnut Walnut Walnut	
	Austrian School	Trinity with Christ Crucified NG 3662	15th C.	1. Red of front wing of angel 2. Red robe L.H. Angel 3. Green dress of R.H. angel	Egg Egg Egg			7
	The Master of Liesborn	The Presentation in the Temple NG 257	2nd half 15th C.	1. Brown-green glaze of tiles 2. Dark grey of arch top R.H.S.	Oil Oil	1.45 1.8	Linseed Linseed	
	Circle of the Master of Liesborn	Ss. Ambrose, Exuperius and Jerome. NG 254	2nd half 15th C.	1. Red of S. Jerome's robe 2. Grey pillar 3. Red of S. Ambrose's robe (red lake glaze)	Oil + egg Oil Oil	3.0 1.76	Walnut Linseed	
Master of the Life of the Virgin		Ss. Jerome, Bernard, Giles and Benedict. NG 250	2nd half 15th C.	1. Grey-white robe of Saint, R.H.S. 2. Black robe 3. Blue sky	Oil Oil (+ egg?) Oil (+ egg?)	3.4	Walnut	8
	The Conversion of S. Hubert. NG 252	2nd half 15th C.	1. White of sleeve 2. Brown horse 3. Green trees	Oil Oil Oil	1.93 2.22 3.23	Linseed ? Walnut?		
	The Mass of S. Hubert. NG 253	1485-1490	1. Green L.H. edge 2. White of altar cloth 3. Red cloak, L.H. figure	Oil Oil Oil	4.02 4.48 3.0	Poppy Poppy ?		

Artist	Picture	Date	Sample	Medium	P/S	Oil type	Note
Master of the S. Bartholomew Altarpiece	Ss. Peter and Dorothy. NG 707	Late 15th early 16th C.	1. White of sky 2. Green brocade	Lean oil Lean oil			9
Master of S. Giles	The Mass of S. Giles NG 4681	c. 1500	1. Green drape, L.H.S. 2. Blue robe of king 3. White altar cloth 4. Red of carpet	Oil + egg Oil + egg Oil + egg Oil + egg			10
	S. Giles and the Hind. NG 1419	c. 1500	1. Grisaille on reverse, grey-white of S. Peter's head 2. Pale blue sky 3. Green foliage, bottom edge 4. Red of cloak	Oil Oil Oil Oil	3·10 3·32 3·33 3·38	Walnut Walnut Walnut Walnut	
Master of Delft	Scenes from the Passion. NG 2922	early 16th C.	1. Grisaille on reverse. Virgin's robe. L.H. wing 2. Grisaille on reverse brown niche. L.H. wing 3. White tail of horse L.H. wing 4. Green of sky, Top R.H. edge, R.H. wing 5. Grisaille of R.H. wing, niche	Oil (+ egg?) Oil (+ egg?) Oil (+ egg?) Oil (+ egg?) Oil (+ egg?)	(1·95) (2·17) (2·10) (2·00) (2·20)		11
Gossaert	The Adoration of the Kings. NG 2790	1st quarter 16th C.	1. Angel's green robe 2. Virgin's blue robe 3. Red of wing of upper L.H. angel 4. Grey-white of masonry 5. Blue grey of ditto	Oil Oil Oil Oil Oil	1·86 1·81 1·85 1·81 1·87	Linseed Linseed Linseed Linseed Linseed	
Carel Fabritius	Self Portrait NG 4042	1654	1. White cloud R.H.S. 2. Blue of sky R.H.S.	Oil Oil	1·60 1·45	Linseed Linseed	
Gerrit Heda	Still Life NG 1469	1640s	1. Black paint 2. White tablecloth	Oil Oil	1·65 1·78	Linseed Linseed	
Rembrandt	Hendrickje Stoffels NG 6432	1659	1. Red background L.H. edge 2. White highlight of robe.	Oil Oil	3·10 3·30	Walnut Walnut	
Van Dyke (style of)	Two Englishmen NG 3605	17th C.	1. Brown velvet tunic 2. Snuff-coloured drape 3. White highlight of satin	Oil Oil Oil	1·41 2·45 1·9	Linseed Walnut Linseed	
Reynolds	General Sir Banastre Tarleton NG 5958	18th C.	1. Red/brown of L.H. drape 2. White of cloud 3. Beige of cloud edge 4. Brown rocks 5. White highlight	Oil Oil Oil Oil + resin Oil + resin	1·75 2·73 3·80 1·86 2·5		12

Notes to the Table

1 Two samples analysed.

2 Two samples analysed.

3 This painting seems to be predominantly in egg-tempera with the possible use of some oil in scumbles.

4 The fatty acid content of these samples was very low though somewhat higher in the first than the other two. Oil is definitely absent and the results are more in accord with glue-tempera than egg-tempera. The use of the latter in some of the thicker, more substantial paint is possible, however.

5 For a description of the possible extent of overpainting in this picture see The National Gallery, Jan 1973–June 1975 (1975), 67.

6 See separate article in this Bulletin.

7 The three samples were very small but definitely showed the absence of oil. The fatty acid levels were very low, resulting most plausibly from lean egg-tempera.

8 The very varied results in these three paintings cannot be rationalised at present. The high P/S ratios of the Mass of S. Hubert seem strongly to suggest the use of poppy oil. The various lower figures for the other samples probably result from mixtures of oils.

9 Very small samples made measurement of the P/S ratios unreliable.

10 See pp. 49–56 this Bulletin.

11 The azelate peaks in all samples were somewhat lower than normal for oil alone, about 75% of the level of palmitate. The medium is therefore probably predominantly linseed oil with some egg but whether the latter is admixed or present in separate layers has not been determined as yet.

12 These very varied ratios perhaps reflect Reynolds's experimental approach to painting. Samples 3 and 4 were found to contain diterpenoid conifer resin components but the particular resin cannot be specified.